Electronic Supporting Information

Discrimination of mechanism of CH_4 formation in Fischer-Tropsch synthesis on Co catalysts: A combined approach of DFT, kinetic analysis and kinetic isotope effect

Yanying Qi[a], Jia Yang[a,b], Xuezhi Duan[a,c], Yi An Zhu[c], De Chen[a]*, Anders Holmen[a]*

[a]Department of Chemical Engineering, Norwegian University of Science and Technology, Sem Sælands vei 4, N-7491 Trondheim, Norway

[b]SINTEF Materials and Chemistry, N-7463 Trondheim, Norway

[c]State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China

Corresponding authors: chen@chemeng.ntnu.no; anders.holmen@chemeng.ntnu.no

S1. The formulas for KIE calculation[1]

Reaction rate is given:

$$r_{AB} = \frac{k_B T}{h} \exp\left(\frac{\Delta S^{0TS-IS}}{R}\right) \exp\left(-\frac{\Delta H^{0TS-IS}}{k_B T}\right) n_A n_B \qquad \text{(S1.1)}$$

Kinetic isotope effect (KIE) is described as:

$$\frac{k_H}{k_D} = \frac{A_H}{A_D} \frac{\Omega_H}{\Omega_D} \qquad \text{(S1.2)}$$

Zero point energy (ZPE) contribution to KIE (H/D) is:

$$\frac{\Omega_H}{\Omega_D} = \exp\left((-1)^{\frac{\left(\left(ZPE_H^{TS} - ZPE_H^{IS}\right) - \left(ZPE_D^{TS} - ZPE_D^{IS}\right)\right)}{k_B T}}\right) \qquad \text{(S1.3)}$$

Entropic contribution to KIE (H/D) (Pre-exponential factor) is obtained by:

$$\frac{A_H}{A_D} = \exp\left(\frac{\left(\left(S_H^{TS} - S_H^{IS}\right) - \left(S_D^{TS} - S_D^{IS}\right)\right)}{R}\right) \qquad \text{(S1.4)}$$

ΔH is approximated by the energy ΔE, which is calculated from DFT. The barriers without zero point correction are identical for H and D, so the barrier term in the KIE only includes the zero point energy corrections. The $k_B T/h$ term is neglected because it does not change for H and D.

Equilibrium isotope effect (IE) is represented as:

$$\frac{K_{eq}^H}{K_{eq}^D} = \exp\left[\frac{-1}{RT}\left(\Delta H^{FS-IS} - T\Delta S^{FS-IS}\right)\right] \qquad \text{(S1.5)}$$

$$\frac{K_{eq}^H}{K_{eq}^D} = \left[\frac{K_{eq}^H}{K_{eq}^D}\right]^{ZPE} \bullet \left[\frac{K_{eq}^H}{K_{eq}^D}\right]^{S} \qquad \text{(S1.6)}$$

ZPE contribution to IE (H/D) is described by:

$$\left[\frac{K_{eq}^H}{K_{eq}^D}\right]^{ZPE} = \exp\left((-1)^{\frac{\left(ZPE_H^{FS} - ZPE_H^{IS}\right) - \left(ZPE_D^{FS} - ZPE_D^{IS}\right)}{k_B T}}\right) \qquad \text{(S1.7)}$$

Entropic contribution to IE (H/D)

$$\left[\frac{K_{eq}^H}{K_{eq}^D}\right]^{S} = \exp\left(\frac{\left(S_H^{FS} - S_H^{IS}\right) - \left(S_D^{FS} - S_D^{IS}\right)}{R}\right) \qquad \text{(S1.8)}$$

All the zero point energy and entropy are calculated from DFT.

TS transition state

IS initial state

FS final state

T reaction temperature

k_B Boltzmann constant

R ideal gas constant

References

(1) Ojeda, M.; Li, A. W.; Nabar, R.; Nilekar, A. U.; Mavrikakis, M.; Iglesia, E. J Phys Chem C 2010, 114, 19761.

Table S1: A complete list of all the direct reaction mechanisms.

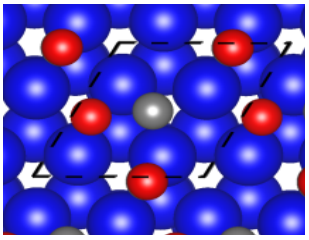
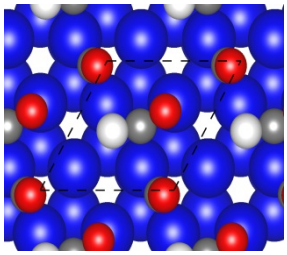
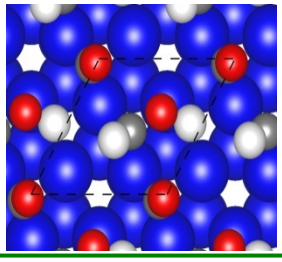
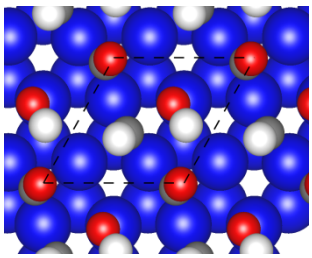
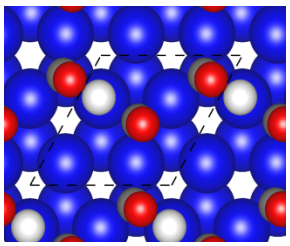
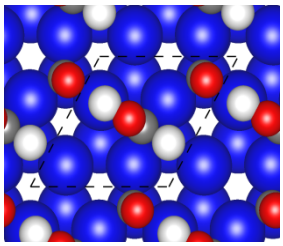
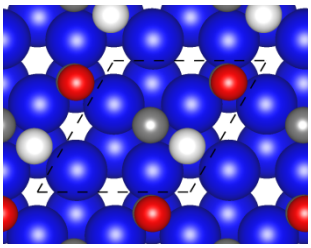
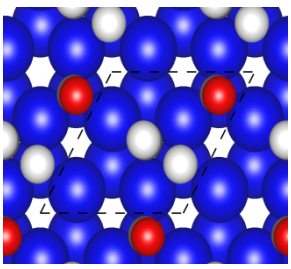
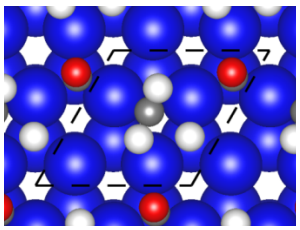
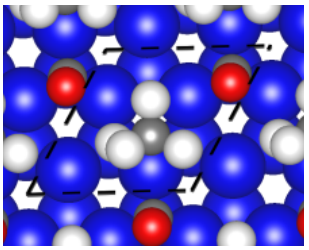
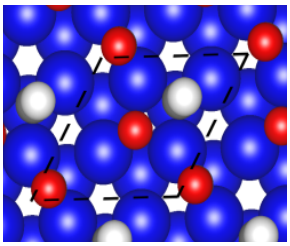
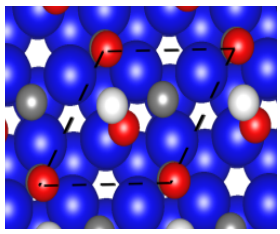
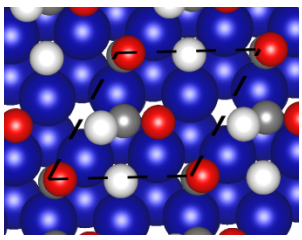
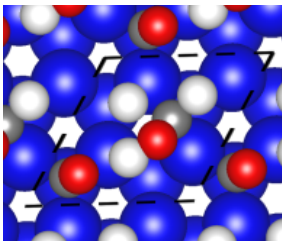
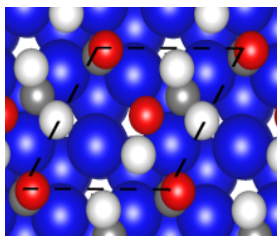
$M_1 = s_1+3s_2+s_3+s_{16}+s_{17}+s_{18}+s_{19}+s_{20}+s_{21}$
$M_2 = s_1+3s_2+s_{10}+s_{11}+s_{17}+s_{18}+s_{19}+s_{20}+s_{21}$
$M_3 = s_1+3s_2+s_4+s_5+s_{16}+s_{17}+s_{18}+s_{19}+s_{21}$
$M_4 = s_1+3s_2+s_{10}+s_{12}+s_7+s_{17}+s_{18}+s_{19}+s_{21}$
$M_5 = s_1+3s_2+s_4+s_6+s_7+s_{17}+s_{18}+s_{19}+s_{21}$
$M_6 = s_1+3s_2+s_{10}+s_{13}+s_{15}+s_{18}+s_{19}+s_{20}+s_{21}$
$M_7 = s_1+3s_2+s_{10}+s_{13}+s_{14}+s_9+s_{18}+s_{19}+s_{21}$
$M_8 = s_1+3s_2+s_{10}+s_{12}+s_8+s_9+s_{18}+s_{19}+s_{21}$
$M_9 = s_1+3s_2+s_4+s_6+s_8+s_9+s_{18}+s_{19}+s_{21}$

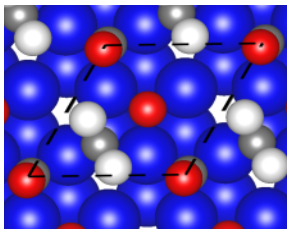
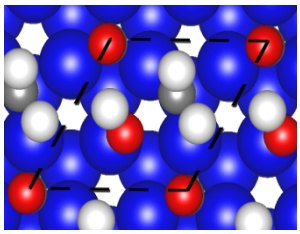
Table S2: Geometric information of the species in elementary steps

$CO^* + * \rightarrow C^* + O^*$			
	d_{C-O}		
Transition state	1.82		
Final state	2.52		
$CO^* + H^* \rightarrow HCO^*$			
	d_{C-H}	d_{C-O}	θ_{O-C-H}
Transition state	1.14	1.26	120.6
Final state	1.10	1.29	115.8
$HCO^* + H^* \rightarrow HCOH^*$			
	d_{O-H}	d_{C-O}	θ_{C-O-H}
Transition state	1.35	1.34	113.2
Final state	1.00	1.34	114.6
$HCO^* + H^* \rightarrow CH_2O^*$			
	d_{C-H}	d_{C-O}	θ_{O-C-H}
Transition state	1.91	1.36	111.0
Final state	1.10	1.38	112.2
$CH_2O^* + * \rightarrow CH_2^* + O^*$			
	d_{C-H}	d_{C-O}	θ_{O-C-H}
Transition state	1.1	1.96	86.8
Final state	1.10	2.73	107.4
$HCO^* + * \rightarrow CH^* + O^*$			
	d_{C-H}	d_{C-O}	θ_{O-C-H}
Transition state	1.10	1.77	98.1
Final state	1.10	2.56	95.7
$HCOH^* + H^* \rightarrow CH_2OH^* + *$			
	d_{C-H}	d_{C-O}	θ_{C-O-H}
Transition state	1.44	1.35	113.4
Final state	1.09	1.36	106.4
$CH_2O^* + H^* \rightarrow CH_2OH^*$			
	d_{O-H}	d_{C-O}	θ_{C-O-H}
Transition state	1.31	1.42	129.5
Final state	0.99	1.36	106.4
$CH_2OH^* + * \rightarrow CH_2^* + OH^*$			
	d_{O-H}	d_{C-O}	θ_{H-C-O}
Transition state	0.98	2.06	97.2
Final state	0.98	2.72	141.0
$HCOH^* \rightarrow CH^* + OH^*$			
	d_{O-H}	d_{C-O}	d_{C-H}

Transition state	0.98	2.05	1.10
Final state	0.98	2.53	1.10
CO* + H* → COH*			
	d_{O-H}	d_{C-O}	θ_{C-O-H}
Transition state	1.97	1.21	56.7
Final state	1.01	1.30	109.3
COH* + * → C* + OH*			
	d_{O-H}	d_{C-O}	θ_{C-O-H}
Transition state	0.98	1.99	103.8
Final state	0.98	2.53	95.7
COH* + H* → HCOH*			
	d_{C-H}	d_{C-O}	θ_{O-C-H}
Transition state	1.12	1.33	113.8
Final state	1.10	1.34	114.3
C* + H* → CH* + *			
	d_{C-H}	d_{C-Co}	
Transition state	1.38	1.81,1.74	
Final state	1.10	1.86	
CH* + H* → CH_2* + *			
	d_{C-H}	d_{C-Co}	
Transition state	1.10,1.43	1.91,1.91,1.84	
Final state	1.10,1.40	1.92,1.92,2.07	
CH_2* + H* → CH_3* + *			
	d_{C-H}	d_{C-Co}	
Transition state	1.58	1.91	
Final state	1.10	2.15	
CH_3* + H* → CH_4* + *			
	d_{C-H}	d_{C-Co}	
Transition state	1.58	2.18	
Final state	1.10	--	

Table S3: Structure information of the transition states for the elementary steps. The big blue balls are Co atoms, the gray ones are C atoms, the red ones are O atoms, and the white ones are H atoms

$CO^* + * \rightarrow C^* + O^*$	$CO^* + H^* \rightarrow HCO^*$	$HCO^* + H^* \rightarrow HCOH^*$
		
$HCOH^* + * \rightarrow HC^* + OH^*$	$CO^* + H^* \rightarrow COH^*$	$COH^* + H^* \rightarrow HCOH^*$
		
$C^* + H^* \rightarrow CH^* + *$	$CH^* + H^* \rightarrow CH_2^* + *$	$CH_2^* + H^* \rightarrow CH_3^* + *$
		
$CH_3^* + H^* \rightarrow CH_4 + *$	$HCO^* + * \rightarrow CH^* + O^*$	$COH^* + * \rightarrow C^* + OH^*$
		
$HCO^* + H^* \rightarrow CH_2O^*$	$HCOH^* + H^* \rightarrow CH_2OH^*$	$CH_2O^* + H^* \rightarrow CH_2OH^*$
		

$CH_2O^* + * \rightarrow CH_2^* + O^*$	$CH_2OH^* + * \rightarrow CH_2^* + OH^*$	
		

S2. The details for the calculations of the free energy

Firstly, the equation to calculate the free energy is defined as shown.

$$G = E + E_{ZPE} + \Delta H^o(0 \rightarrow T) - TS$$

Where G is free energy, E refers to electronic energy determined by DFT, E_{ZPE} is zero point energy.

$$E_{ZPE} = \sum_{i=1}^{3N-6(5)} \frac{N_A h v_i}{2}$$

Where N_A and h refers to Avogadro's number and Plank's constant, and v_i and N is the frequency of the normal mode and the number of atoms.

The evaluation of enthalpy (H) and entropy (S) were shown below.

As for the adsorbates, the enthalpy (H) is equal to the internal energy (U) with neglecting the PV contributions. It has two solutions according to the intensity of adsorption.

For weakly adsorbed species, we may assume to a first approximation that they behave as two-dimensional gases and maintain all rotational and vibrational modes of the corresponding gaseous species. So the standard internal energy and the entropy change of adsorption is calculated according to

$$\Delta U^{o}_{trans,\,2D}(0 \rightarrow T) - \Delta U^{o}_{trans,3D}(0 \rightarrow T) = -\frac{1}{2}RT$$

$$\Delta S = S_{trans,2D} - S_{trans,\,3D} = R\left[ln\left(\frac{\frac{h}{k_B T}}{(2\pi m k_B T)^{1/2}}\left(\frac{SA}{N_{sat}}\right)P^0\right) - \frac{1}{2}\right]$$

Where SA/N_{sat} refers to the area occupied per adsorbed molecule at the standard state conditions. Generally the standard state is assumed to be monolayer coverage and SA/N_{sat} is equal to the reciprocal of the surface concentration of sites.

For strongly adsorbed species, the frustrated translational and rotational modes are treated as special cases of vibrational modes. Accordingly, the entropy and the internal energy is evaluated according to the following equations.

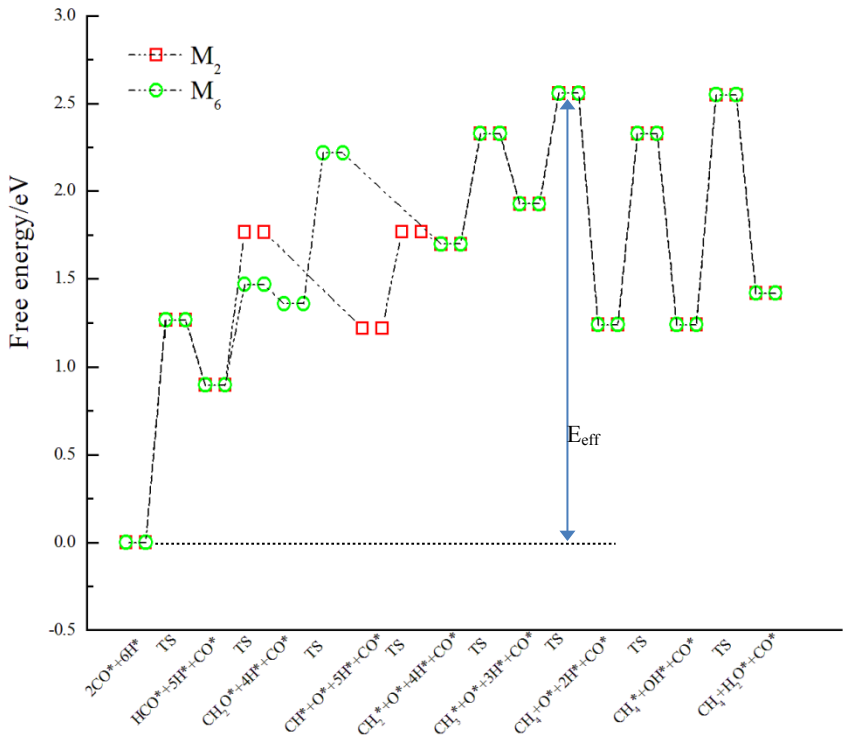
$$\Delta U^0(0 \rightarrow T) = U_{vib} = R\sum_i^{3N} \frac{x_i T}{e^{x_i} - 1}$$

$$S = S_{vib} = R\sum_i^{3N}\left(\frac{x_i}{e^{x_i} - 1} - ln\left(1 - e^{-x_i}\right)\right)$$

$$\Delta H(T) = H_{tran} + H_{rot} + \Delta H_{vib} = \frac{5}{2}RT + \frac{3}{2}RT + R\sum_{i}^{3N}\frac{x_i T}{e^{x_i} - 1}$$

Where $x_i = \frac{hc}{k_B T \lambda_i}\frac{1}{}$, c and k_B refer to speed of light and Boltzmann constant, $1/\lambda i$ is wavenumber corresponding to each vibrational frequency.

(a)



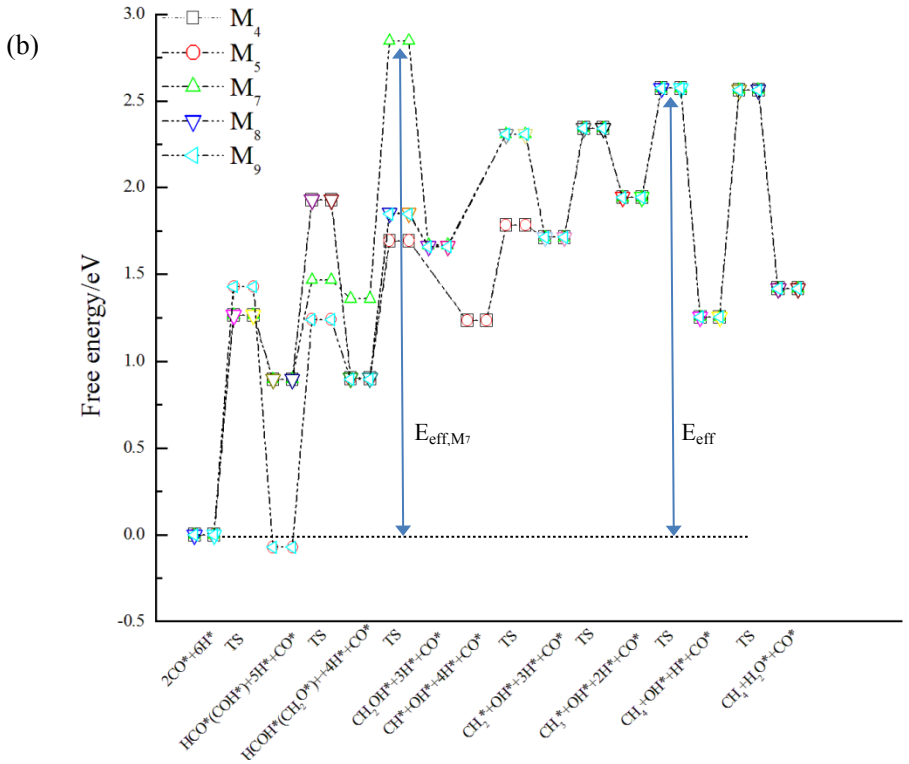


Fig. S1 The potential energy profiles for different reaction mechanisms of methane formation on 0.25 ML CO pre-covered Co(0001) surface.M_2 and M_6 are illustrated in (a), and M_4, M_5, M_7, M_8 and M_9 are illustrated in (b). The free energies are given in eV with respect to adsorbed species 2CO*+6H*, where the addition of CO was presented as pre-adsorbed CO. This plot has been constructed using DFT calculations and normal-mode analysis for the total free energy at 483K

S3. Derivation of rate expressions for different mechanisms.

Mechanism 2

$CO + * \leftrightarrow CO*$ [1]

$H_2 + 2* \leftrightarrow 2H*$ [2]

$CO* + H* \leftrightarrow HCO* + *$ [3]

$HCO* + * \rightarrow CH* + O*$ [4]

$CH* + H* \leftrightarrow CH_2*$

$CH_2* + H* \leftrightarrow CH_3*$

$CH_3* + H* \leftrightarrow CH_4*$

.....

$O* + H* \leftrightarrow OH* + *$ [5]

$OH* + H* \leftrightarrow H_2O + 2*$ [6]

The fourth step is assumed as the rate determining step, and other steps before RDS are equilibrium.

$$\theta_{CO} = K_{CO} P_{CO} \theta_*$$

$$\theta_H = \sqrt{K_{H_2} P_{H_2}}\, \theta_*$$

$$\theta_{HCO} = \frac{K_3 \theta_{CO} \theta_H}{\theta_*} = K_3 K_{CO} P_{CO} \sqrt{K_{H_2} P_{H_2}} \theta_*$$

$$r = k_4\theta_{HCO}\theta_* = k_4K_3K_{CO}P_{CO}\sqrt{K_{H_2}P_{H_2}}\theta_*^2$$

Apply site conservation
$\theta_{CO} + \theta_H + \theta_{HCO} + \theta_* = 1$

Assuming the site coverage of HCO* is negligible compared with CO* and H*, the expression for vacant site can be simplified as

$$\theta_* = \frac{1}{1 + K_{CO}P_{CO} + \sqrt{K_{H_2}P_{H_2}}}$$

The rate expression is therefore obtained:

$$r = \frac{k_4K_3K_{CO}P_{CO}\sqrt{K_{H_2}P_{H_2}}}{\left(1 + \sqrt{K_{H_2}P_{H_2}} + K_{CO}P_{CO}\right)^2}$$

Mechanism 4, 5

CO + *↔ CO*	[1]
H_2 + 2*↔ 2H*	[2]
CO* + H*↔ HCO* + *	[3]
Or CO* + H*↔ COH* + *	[3']
HCO* + H* ↔ HCOH* + *	[4]
Or COH* + H* ↔ HCOH* + *	[4']
HCOH* + * ↔ CH* + OH*	[5]

CH* + H* ↔ CH_2*
CH_2* + H* ↔ CH_3*
CH_3* + H* ↔ CH_4*
.....
OH* + H* ↔ H_2O + 2*

The fifth step is the rate determining step, and other steps before the RDS are all in equilibrium.

$$\theta_H = \sqrt{K_{H_2}P_{H_2}}\theta_*$$

$$\theta_{CO} = K_{CO}P_{CO}\theta_*$$

$$\theta_{HCO} or \theta_{COH} = \frac{K_3\theta_{CO}\theta_H}{\theta_*} = K_3K_{CO}P_{CO}\sqrt{K_{H_2}P_{H_2}}\theta_*$$

Apply pseudo steady-state theory for HCOH species.

$$k_4\theta_{HCO}\theta_H - k_{-4}\theta_{HCOH}\theta_* = 0$$

$$\theta_{HCOH} = K_4K_3K_{CO}P_{CO}K_{H_2}P_{H_2}\theta_*$$

The reaction rate based on the proposed RDS can be expressed as follow:

$$r = k_4\theta_{HCOH}\theta_* = k_4K_3K_{CO}K_{H_2}P_{CO}P_{H_2}\theta_*^2$$

Apply site conservation

$$\theta_* + \theta_{CO} + \theta_H + \theta_{HCO} + \theta_{HCOH} = 1$$

$$\theta_* = \frac{1}{1 + K_{CO}P_{CO} + \sqrt{K_{H_2}P_{H_2}} + K_3K_{CO}P_{CO}\sqrt{K_{H_2}P_{H_2}} + K_4K_3K_{CO}P_{CO}K_{H_2}P_{H_2}}$$

Assuming the site coverage of CHO* and HCOH* are negligible compared with CO* and H*, the expression for vacant site can be simplified as

$$\theta_* = \frac{1}{1 + K_{CO}P_{CO} + \sqrt{K_{H_2}P_{H_2}}}$$

The rate expression is therefore obtained:

$$r = k_5\theta_{HCOH}\theta_* = \frac{k_5K_4K_3K_{CO}K_{H_2}P_{CO}P_{H_2}}{(1 + K_{CO}P_{CO} + \sqrt{K_{H_2}P_{H_2}})^2}$$

Mechanism 6

$CO + * \leftrightarrow CO*$ [1]
$H_2 + 2* \leftrightarrow 2H*$ [2]
$CO* + H* \leftrightarrow HCO* + *$ [3]
$HCO* + H* \leftrightarrow CH_2O* + *$ [4]
$CH_2O* + H* \rightarrow CH_2* + *$ [5]
$CH_2* + H* \leftrightarrow CH_3*$
$CH_3* + H* \leftrightarrow CH_4*$
.....
$O* + H* \leftrightarrow OH* + *$
$OH* + H* \leftrightarrow H_2O + 2*$

The fifth step is rate determining step, and other steps before RDS are equilibrium.

$\theta_{CO} = K_{CO}P_{CO}\theta_*$

$\theta_H = \sqrt{K_{H_2}P_{H_2}}\,\theta_*$

$\theta_{HCO} = \frac{K_3\theta_{CO}\theta_H}{\theta_*} = K_3K_{CO}P_{CO}\sqrt{K_{H_2}P_{H_2}}\theta_*$

$\theta_{CH_2O} = \frac{K_4\theta_{HCO}\theta_H}{\theta_*} = K_4K_3K_{CO}K_{H_2}P_{CO}P_{H_2}\theta_*$

$r = k_5\theta_{CH_2O}\theta_* = k_5K_4K_3K_{CO}K_{H_2}P_{CO}P_{H_2}\theta_*^2$

Apply site conservation

$\theta_{CO} + \theta_H + \theta_{HCO} + \theta_{CH_2O} + \theta_* = 1$

Assuming the site coverage of HCO* and CH_2O* are negligible compared with CO* and H*, the expression for vacant site can be simplified as

$$\theta_* = \frac{1}{1 + K_{CO}P_{CO} + \sqrt{K_{H_2}P_{H_2}}}$$

The rate expression is therefore obtained:

$$r = \frac{k_5 K_4 K_3 K_{CO} K_{H_2} P_{CO} P_{H_2}}{\left(1 + \sqrt{K_{H_2}P_{H_2}} + K_{CO}P_{CO}\right)^2}$$

Mechanism 8, 9

CO + *↔ CO*	[1]
H_2 + 2*↔ 2H*	[2]
CO* + H*↔ HCO* + *	[3]
Or CO* + H*↔ COH* + *	[3']
HCO* + H* ↔ HCOH* + *	[4]
Or COH* + H* ↔ HCOH* + *	[4']
HCOH* + H* → CH_2OH* + *	[5]
CH_2OH* + * ↔ CH_2* + OH*	[6]

CH_2* + H* ↔ CH_3*

CH_3* + H* ↔ CH_4*

.....

OH* + H* ↔ H_2O + 2*

The sixth step is rate determining step, and other steps before RDS are equilibrium.

$$\theta_{CO} = K_{CO}P_{CO}\theta_*$$

$$\theta_H = \sqrt{K_{H_2}P_{H_2}}\,\theta_*$$

$$\theta_{HCO} = \frac{K_3\theta_{CO}\theta_H}{\theta_*} = K_3K_{CO}P_{CO}\sqrt{K_{H_2}P_{H_2}}\theta_*$$

$$\theta_{HCOH} = \frac{K_4\theta_{HCO}\theta_H}{\theta_*} = K_4K_3K_{CO}K_{H_2}P_{CO}P_{H_2}\theta_*$$

$$\theta_{CH_2OH} = \frac{K_5\theta_{HCOH}\theta_H}{\theta_*} = K_5K_4K_3K_{CO}P_{CO}\left(K_{H_2}P_{H_2}\right)^{1.5}\theta_*$$

$$r = k_6\theta_{CH_2OH}\theta_* = k_6K_5K_4K_3K_{CO}P_{CO}\left(K_{H_2}P_{H_2}\right)^{1.5}{\theta_*}^2$$

Apply site conservation

$$\theta_{CO} + \theta_H + \theta_{HCO} + \theta_{HCOH} + \theta_{CH_2OH} + \theta_* = 1$$

Assuming the site coverage of HCO*, HCOH* and CH_2OH* are negligible compared with CO* and H*,

the expression for vacant site can be simplified as

$$\theta_* = \frac{1}{1 + K_{CO}P_{CO} + \sqrt{K_{H_2}P_{H_2}}}$$

The rate expression is therefore obtained:

$$r = \frac{k_6 K_5 K_4 K_3 K_{CO} P_{CO} \left(K_{H_2} P_{H_2}\right)^{1.5}}{\left(1 + \sqrt{K_{H_2} P_{H_2}} + K_{CO} P_{CO}\right)^2}$$

Table S4: Vibrational frequencies (cm^{-1}) for the adsorbed species in elementary steps

	C* + H* → CH* + *																				
TS-H	1805	1474	763	604	545	455	372	333	291	179	130	-662									
TS-D	1805	1052	598	571	543	433	372	332	291	178	130	-471									
IS-H	1850	1214	1109	680	642	552	448	387	325	318	189	87									
IS-D	1850	861	785	641	550	501	430	387	325	318	189	87									
	$CH^* + H^* \rightarrow CH_2^* + *$																				
TS-H	3052	1761	1433	959	866	797	670	429	385	378	337	278	181	95	-438						
TS-D	2248	1761	1020	728	618	613	596	408	385	373	320	278	181	95	-317						
IS-H	3047	1803	1186	1047	818	801	705	657	447	388	378	352	329	195	77						
IS-D	2244	1803	839	743	662	593	592	504	415	388	372	352	316	195	77						
	$CH_2^* + H^* \rightarrow CH_3^* + *$																				
TS-H	3016	2957	1707	1571	1353	977	932	575	559	479	400	386	376	357	220	200	103	-785			
TS-D	2225	2147	1707	1114	989	727	675	510	436	394	384	374	354	328	210	198	98	-569			
IS-H	3019	2662	1745	1416	1383	1063	980	925	668	614	543	497	423	393	366	238	201	57			
IS-D	2217	1942	1745	1012	1000	753	712	695	546	508	456	429	410	393	365	237	176	57			
	$CH_3^* + H^* \rightarrow CH_4$																				
TS-H	3136	3109	3008	1717	1639	1398	1380	1188	897	767	641	443	368	351	346	311	277	249	144	120	-828
TS-D	2323	2300	2149	1712	1163	1014	1000	881	658	557	463	439	358	329	311	270	248	232	134	113	-603
IS-H	3105	3039	2923	1797	1388	1368	1319	1246	1181	718	680	553	451	439	391	339	307	266	240	157	103
IS-D	2299	2225	2107	1796	1010	990	934	882	880	531	486	468	411	374	334	307	288	242	228	149	100
	CO* + H* → HCO*																				
TS-H	2496	1835	1429	991	685	478	407	392	339	278	249	188	169	79	-454						
TS-D	1837	1824	1416	797	544	469	406	388	335	271	246	184	169	78	-382						
IS-H	1898	1783	1286	1218	870	433	396	393	359	338	296	265	179	156	87						
IS-D	1898	1783	910	862	616	433	396	393	359	338	296	265	179	156	87						

	HCO* → HC* + O*																				
TS-H	3069	1858	956	844	599	536	462	419	401	391	347	310	222	59	-414						
TS-D	2259	1858	727	638	555	529	453	416	401	370	347	307	222	59	-413						
IS-H	2960	1794	1262	1217	865	535	417	412	378	373	339	236	211	180	85						
IS-D	2176	1793	1254	934	636	488	416	412	377	362	337	235	207	180	85						
	HCO* + H* → HCOH*																				
TS-H	2968.14	1783.15	1265.13	1233	1107	836	731	525	477	427	379	360	313	269	206	182	74	-1401			
TS-D	2178.95	1782.15	1088.47	940	892	635	561	473	461	416	373	356	302	267	200	181	74	-1019			
IS-H	2957.73	1797.23	1422.35	1315	1227	1192	953	852	524	449	419	381	365	312	278	216	171	80			
IS-D	2174.4	1797.08	1305.05	1006	930	850	675	630	480	446	419	374	360	310	277	213	170	80			
	HCO* + H* → CH_2O*																				
TS-H	3518	2572	1761	1280	1137	1061	716	586	472	436	417	390	284	261	184	115	55	-458			
TS-D	2558	1877	1758	1145	990	787	573	549	428	416	395	365	258	252	177	111	54	-401			
IS-H	2958	1797	1422	1315	1227	1192	953	852	524	449	419	381	365	312	278	216	171	80			
IS-D	2174	1797	1305	1006	930	850	675	630	480	446	419	374	360	310	277	213	170	80			
	HCOH* → CH* + OH*																				
TS-H	3608	3068	1760	909	839	751	673	639	525	442	414	399	384	280	190	160	87	-354			
TS-D	2626	2261	1758	690	657	625	551	514	442	435	410	390	380	273	185	154	87	-353			
IS-H	3206	2843	1631	1388	1246	1178	966	708	488	467	425	401	337	289	247	213	162	99			
IS-D	2342	2085	1628	1182	1041	906	712	521	463	453	423	384	337	278	246	210	159	96			
	HCOH* + H* → CH_2OH*																				
TS-H	3074	2951	1960	1599	1416	1265	1126	978	737	650	497	458	454	398	342	312	280	219	161	121	-658
TS-D	2249	2165	1594	1392	1135	1050	915	727	550	499	473	449	426	362	337	301	269	215	157	118	-494
IS-H	3228	2876	1636	1402	1384	1243	1179	1110	975	904	709	508	476	418	399	324	300	245	223	165	129
IS-D	2357	2110	1633	1184	1041	991	903	786	718	641	522	475	464	416	384	323	289	243	220	162	126
	CH_2O* + H* → CH_2OH*																				
TS-H	3060	2978	1756	1399	1177	1152	1090	914	791	659	499	459	397	395	373	291	268	236	177	109	-1385
TS-D	2272	2153	1752	1038	923	890	832	767	589	503	473	437	393	387	361	289	242	230	171	107	-997

IS-H	3057	2972	1784	1455	1418	1169	1163	1146	995	938	702	476	447	408	393	381	330	266	261	179	144
IS-D	2274	2147	1783	1115	1023	975	888	824	816	666	516	455	442	403	385	373	326	258	240	175	142
	$CO^* + H^* \rightarrow COH^*$																				
TS-H	1735	1582	1127	556	438	385	368	348	299	271	266	226	150	132	-1522						
TS-D	1723	1515	837	458	438	381	348	346	298	266	247	223	149	130	-1126						
IS-H	1897	1783	1286	1218	870	433	396	393	359	338	296	265	179	156	87						
IS-D	1897	1783	910	862	616	433	396	393	359	338	296	265	179	156	87						
	$COH^* + H^* \rightarrow HCOH^*$																				
TS-H	2966	2719	1619	1405	1247	1146	880	632	423	417	383	320	288	262	180	134	84	-361			
TS-D	2175	1986	1609	1228	1038	870	634	511	423	415	382	311	272	255	175	131	79	-334			
IS-H	2859	1678	1329	1253	1197	1138	786	696	525	440	407	397	370	329	251	197	142	101			
IS-D	2093	1662	1327	951	849	805	559	515	512	438	401	393	366	318	242	196	141	101			
	$COH^* \rightarrow C^* + OH^*$																				
TS-H	3542	1756	796	701	604	581	423	393	361	339	272	199	155	131	-389						
TS-D	2578	1754	613	593	576	497	417	387	361	332	271	197	153	131	-385						
IS-H	2977	1679	1319	1240	655	470	425	389	387	364	315	259	169	167	146						
IS-D	2174	1668	1318	938	491	458	421	389	369	359	315	252	168	166	145						
	$CH_2O^* \rightarrow CH_2^* + O^*$																				
TS-H	3081	3012	1753	1356	1025	761	606	532	480	433	390	358	356	289	201	166	152	-358			
TS-D	2283	2180	1753	995	763	562	498	473	440	428	388	357	353	283	197	165	146	-347			
IS-H	3039	2955	1751	1417	1167	1138	981	653	472	435	402	392	361	342	262	249	177	156			
IS-D	2259	2134	1750	1098	975	887	812	483	443	428	401	381	359	338	246	241	170	153			
	$CH_2OH^* \rightarrow CH_2^* + OH^*$																				
TS-H	3576	3059	2801	1683	1374	889	791	750	655	590	432	412	382	375	369	360	245	192	157	135	-432
TS-D	2602	2251	2041	1680	1006	649	580	557	513	470	415	398	361	358	342	322	240	190	151	131	-429
IS-H	3280	3105	2991	1637	1417	1403	1186	1134	964	779	598	448	359	350	314	304	254	207	142	114	84
IS-D	2390	2305	2167	1628	1149	1075	991	828	756	569	470	422	353	334	311	290	228	201	139	111	81

Table S5: Chemisorption energies of CO, atomic H and COH at different unit cell size

species	2×2	3×3
CO -fcc	-1.70 eV	-1.70 eV
H -fcc	-2.85 eV	-2.79 eV
COH -hcp	-4.35 eV	-4.29 eV